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Effect of pore structure on catalytic properties of mesoporous silica supported rhodium catalysts for the hydrogenation of cinnamaldehyde

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ABSTRACT

Rhodium particles for catalyzing the hydrogenation were effectively confined in the mesopores of MCM-41 and MSU-H silica by using supercritical CO₂ as impregnation solvent. It was found that the calcination was an important step to control the size of Rh particles, and its influence was strongly dependent on the pore size distribution of mesoporous silica support. The prepared catalysts were characterized by X-ray diffraction (XRD), nitrogen adsorption, and transmission electron microscopy (TEM). While irregularly big Rh particles were often found on MCM-41 with smaller pore size (2.7 nm) during calcination at 873 K, homogeneous and small Rh particles were maintained inside MSU-H with relatively larger pore size (8.4 nm). The hydrogenation of cinnamaldehyde using the prepared catalysts was carried out in supercritical CO₂. Rh/MSU-H which was calcined at 673 K provided the highest catalytic activity among the studied conditions. The results indicated that the catalyst on the support with larger pore size and smaller size of Rh particles might be desirable to attain higher catalytic activity.

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1. Introduction

Mesoporous silica has gained much interest in the field for the preparation of high-dispersion metal supported catalysts, based on its unique advantages over conventional support materials: (i) high surface area and pore volume facilitate the adsorption and dispersion of metal precursor (ii) intrinsic porosity provides more access to the active center for the substrate (Yang et al., 2012; Chen et al., 2004; Prashar et al., 2011; Lee et al., 2009; Gutiérrez et al., 2013).

Recently, supercritical impregnation method has been reported to be a new method for preparing high-dispersion metal supported catalysts such as mesoporous silica supported catalysts (Gupta et al., 2005; Zhang et al., 2005; Aschenbrenner et al., 2008; Alibouri et al., 2009; Tenorio et al., 2012). Supercritical fluids can dissolve the precursor of target

metal particles and also can transport the dissolved precursor molecules into micro pores due to high diffusivity and low surface tension, which are favorable features for the impregnation of nanoparticles in mesoporous silica and for efficiently utilizing the pores in porous materials. Carbon dioxide can be one of the most suitable supercritical fluids for the above purpose because it is non-toxic, non-reactive, non-flammable, and no-need of drying process. The supercritical impregnation is pointed out to consist of (a) the dissolution of a metallic precursor in supercritical CO₂, and (b) the adsorption of the metallic precursor on the substrate (c) the calcination and reduction of its precursor to its metallic form. Various types of metal supported mesoporous silica have been successfully prepared by supercritical impregnation method (Erkey, 2009, 2011). Our group has also studied the preparation and the activity of mesoporous silica supported cobalt catalysts by

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using supercritical impregnation method, and could obtain highly dispersed cobalt catalysts (Shimizu et al., 2012). However, it has been very limited knowledge about the effect of mesoporous structure on the size and thermal stability of metal nanoparticles supported on mesoporous materials (Morère et al., 2011). Furthermore, it has been a still few reports to investigate catalytic activities of the catalysts prepared by supercritical impregnation method (Erkey, 2009, 2011). Hence, further investigations would be needed for catalytic activities of the catalysts prepared by supercritical impregnation method, and the relationship between the structure of the catalyst and the catalytic activity.

Much attention has been paid for selective hydrogenation of α , β -unsaturated aldehydes owing to their wide applicability in the synthesis of fine chemicals such as perfumes and pharmaceuticals (Mäki-Arvela et al., 2005; Chatterjee et al., 2003; Wang et al., 2008; Gutiérrez et al., 2013). The selective hydrogenation of cinnamaldehyde (CAL) is a commercially important reaction that produces cinnamyl alcohol (COL), hydrocinnamaldehyde (HCAL) and hydrocinnamyl alcohol (HCOL). Recently, an important application was found for the hydrocinnamaldehyde, an intermediate in the synthesis of medicines for the treatment of HIV (Muller et al., 1999). Pd and Rh generally exhibit high activity and high selectivity of hydrocinnamaldehyde in catalytic reaction (Bertolini et al., 2013; Zhao et al., 2003; Cabiác et al., 2008; Reyes et al., 2000). During the past few years, several examples of synthesis of mono- or bi-metallic Pd catalysts for selective hydrogenation of CAL to HCAL have been reported (Sairanen et al., 2012; Tessonier et al., 2005; Pham-Huu et al., 2001). On the other hand, few papers have been published concerning the use of Rh for the selective hydrogenation of CAL to HCAL.

In this work, we have focused on mesoporous silica supported Rh catalysts for the hydrogenation CAL prepared by supercritical CO₂ impregnation method with use of two different mesoporous silica supports and also with varying the calcination temperature. The discussion was made to elucidate the effects of pore structure and Rh particle dispersion on catalytic reaction performance.

2. Experimental

2.1. Materials

Rhodium(III) acetylacetonate and mesoporous silica (MCM-41 and MSU-H) were purchased from Aldrich. CO₂ (purity of 99.5%), and H₂ gas (>99.995%) were obtained from Taiyo Nippon Sanso cooperation. All materials were used without further purification.

2.2. Impregnation by supercritical fluid method

Experimental apparatus and procedure by supercritical impregnation method were described in our previous work (Shimizu et al., 2012). In the experiments, Rh(acac)₃ of 0.08 g was introduced into the reactor whose internal volume is 50 cm³. The basket containing 0.5 g of silica was first placed on the aluminum stage in the reactor, and then the reactor was set in the air bath. After the temperature reaching 333 K, CO₂ was pressurized up to 20 MPa using a high-pressure pump. The reaction time was assumed to be the elapsed time after reaching the desired pressure. During the reaction, the reactor contents were mixed mechanically using a magnetic

stirrer. After 24 h, the system was gradually depressurized to atmospheric pressure in order to stop the reaction. All these reaction conditions were selected so as to achieve ca.4 wt% loading of Rh on silica supports. The samples in the basket were collected and calcined in a muffle oven (Muffle Furnace ETR-11K, ISUZU Seisakusyo Co., Ltd.) at 673–873 K and 3 h. The obtained sample was named as Rh/MCM-41(X) or Rh/MSU-H(X), where (X) represents the calcination temperature in kelvin.

2.3. Catalyst characterization

To determine the Rh amount loaded in the mesoporous silica, we used a scanning electron microscope (SEM, JSM-6500F, JEOL Ltd.) attached with an energy-dispersive X-ray spectrometer (EDS) at an operating voltage was 15 kV. We analyzed three points of each Rh-supported silica sample using SEM-EDS, and adopted the average value as a loading amount of Rh, which was confirmed to close to the loading amount estimated by ICP-MS (ICP-QQQ 8800, AGILENT) analysis. The structure of Rh particles after calcination was characterized by using the XRD (Miniflex, RIGAKU). The morphology of samples was analyzed using a field-emission transmission electron microscope (FE-TEM, HF-2000, Hitachi Ltd.). N₂ adsorption isotherms were obtained using a Belsorp-mini instrument (BEL Japan, Inc.). The surface area and total pore volume were calculated by the BET equation and the BJH formula from the adsorption isotherm, respectively.

2.4. Catalytic activities of cinnamaldehyde hydrogenation

The hydrogenation of cinnamaldehyde in supercritical CO₂ solvent was carried out in a 100 cm³ stainless steel batch reactor. Before the experiments of hydrogenation, the obtained catalysts were reduced under H₂ atmosphere at 393 K for 1 h, respectively. After the reduction process, 0.05 g of catalyst and 2.0 g of the reactant were loaded into the reactor. The reactor was sealed, flushed with CO₂ at 2 MPa pressure for three times to remove air and maintained at 323 K for 90 min to stabilize the temperature. H₂ was firstly loaded into the reactor up to 4 MPa. Liquid CO₂ was then charged into the reactor and compressed up to 9–18 MPa using a high-pressure liquid pump. The reactant mixture was stirred continuously with a magnetic stirrer for 3 h. After reaching the reaction time, the reactor was cooled in ice-cold water to quench the reaction. The reaction products were analyzed using a gas chromatography (GC-2014; Shimadzu Corp.) equipped with a FID detector. We also conducted the reaction experiments in organic solvents (ethanol, and hexane) of 18 ml using the same reactor for comparison with the same conditions (amount of cinnamaldehyde, H₂ pressure).

3. Results and discussion

3.1. Catalyst characterization

Table 1 summarizes the measured characteristic properties of the prepared catalysts. The average Rh particle sizes of samples were determined by TEM images, where we checked their validity by comparing the value of Rh/MCM-41(673), 1/6 nm, from TEM image with the value of 1.8 nm from CO adsorption. The Rh loading amount of all samples was confirmed to be about 4 wt% by EDS analyses within an uncertainty of 10%.

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